Sixth Quarterly Report

DEVELOPMENT OF UNIFORM AND PREDICTABLE BATTERY MATERIALS FOR NICKEL-CADMIUM AEROSPACE CELLS

8 December 1969 — 7 March 1970

Contract No. NAS 5-11561

Prepared by

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Waltham, Massachusetts 02154

for

Goddard Space Flight Center
Greenbelt, Maryland

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ABSTRACT

The objective of the current phase of this program is to assess the different methods of impregnation of nickel cadmium battery plates. Weight gain alone is insufficient characterization because of the ill-defined stoichiometry of the active materials (incomplete utilization at the negative and nonintegral stoichiometry at the positive). Analytical methods are therefore required to define distribution and utilization. This report describes the techniques that were established to meet those requirements.

For the negative plates, both the charged and discharged forms of the active material are readily determined since the ionic form [$Cd(OH)_2$] dissolves readily in ammoniacal NH_4Cl whereas cadmium metal is unaffected. After separation, the two forms of cadmium are determined by EDTA titration.

A similar approach to the analysis of the positive electrode results in significant errors due to corrosion of the nickel substrate. A novel approach involving potentiostatic control of the plate during the extraction process successfully eliminated the corrosion problem, but its application is limited to analysis of the plate in the discharged state. For this reason and because both the charged and discharged species are soluble in any extraction solution, a separate determination of the state of charge is necessary. The method used depends on the determination of the active oxygen equivalent by reaction with potassium iodide and subsequent estimation of the iodine formed with sodium thiosulphate. It was established that it is critically important not to wash and dry the electrodes prior to analysis. Plaque corrosion is also another potential source of error in this determination. Specific techniques are described to minimize these errors. However, even with these precautions, determination of the state of charge by a chemical method still gives a figure lower than that defined by discharge. It is concluded, therefore, that the only guide to utilization of positive active material is a measurement of the amount of material that is not

discharged (in terms of residual active oxygen) when the plate is in the nominally discharged state.

The program of impregnation procedures to be carried out is discussed briefly.

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I. INTRODUCTION

This program is concerned with the preparation of uniform and predictable components for sealed NiCd cells. In the first phase of the program, emphasis was placed on defining the critical factors in the preparation of sintered nickel plaque with uniform and reproducible characteristics. The current aspect consists of a study of the precipitation of the active materials of the nickel cadmium cell in the pore structure of the nickel plaque, again in the context of achieving uniform and reproducible behavior.

Two criteria are normally used to assess the effectiveness of impregnation processes. These are weight gain and capacity. For the objectives of this program, these two figures alone are not considered to be sufficient characterization to ensure uniform behavior, particularly as function of cycle life. The problem is associated with the inefficiency of the charge-discharge processes, which can be a function of the morphology of the active materials or their distribution in the plaque structure on a microscopic scale,* i.e., the conditions prevailing during impregnation. The inefficiency may be real in that there is a secondary Faradaic process (e.g., O_2 evolution on charge) or apparent when some of the active material does not cycle. This latter behavior can be a result of electrical isolation, chemical changes, or passivation. It is, therefore, desirable to be able to identify those areas of the plate that do not cycle efficiently in order to be able to identify truly uniform behavior. This information can be obtained by careful chemical analysis of the active materials. It is, of course, necessary to be able to identify the charged and discharged states independently. This is relatively straightforward for the negative plates, but is quite complex for the positives.

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*Macroscopic deviations in the distribution would be apparent from an analysis of the weight gain per unit area of different regions of the plaque.

This report describes the experimental techniques for chemical analysis and gives particular attention to the limitations of each one.

II. CHEMICAL ANALYSIS OF NiCd BATTERY PLATES

The chemical constitution of the active materials of the nickel-cadmium couple were discussed in detail in the previous report.[1] Briefly, the components we are interested in are Cd°, Cd^{2+}, and Ni° (plaque) in the negative plate; and, at the positive, Ni^{2+}, $Ni^{(2+x)+}$,* K^+, H_2O, adsorbed or occluded O_2 and the nickel metal of the plaque. Clearly the positive plate is a much more complicated problem.

Analysis of the negative plate is readily carried out by selective dissolution of cadmium hydroxide with subsequent determination of the amount dissolved by complexometric titration. The metallic residue of cadmium and nickel may be dissolved in nitric acid and the two components of the solution determined again by complexometric titration. Analysis is uncomplicated except for electrodes close to being fully charged, that are difficult to wash and dry without oxidation.

For the positive plate in the green state (prior to formation), the components are Ni^{2+}, Ni°, and water. As will be demonstrated, analysis at this stage is straightforward if certain precautions are taken. In the charged state which is characterized by nonintegral stoichiometry, the value of x in $Ni^{(2+x)+}$ can range from one to nearly two.* Determination of the value of x poses a particular problem in that the highest valent states are stable only in the presence of KOH at the particular concentration at which they were formed. Any dilution of the electrolyte prompts a self discharge reaction coupled with the evolution of oxygen. Thus, although sophisticated methods have been described for determination of the state of charge, e.g., infrared absorption intensities,[2] these do not represent the true value in situ because washing and drying is a necessary precursor to the measurement. This factor will be examined in more detail below. In the discharged state the value of x is never zero, i.e., the plate cannot be reduced to a uniquely divalent state.

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* $Ni^{(2+x)+}$, represents the nonstoichiometric charged state of the positive plate.

Knowledge of the value of x in the discharged state is essential to define the behavior of plates prepared under different circumstances, its determination by any of the methods to be discussed is relatively straightforward since the complication of the self discharge process does not exist.

The residual valence in excess of two can, however, present problems in determining the total quantity of active material in the plate. This occurs because all the methods of determination depend on dissolution by complexation of the nickel in ionic form while leaving the metallic nickel substrate unattacked. However, the substrate is readily attacked in the presence of an electroreducible species such as the residual charged material in the following manner. The presence of residual charge is probably a result of isolation by the completely discharged state $Ni(OH)_2$, a poor electrical conductor; but, as the source of isolation is dissolved, the electroreducible species is exposed. Simultaneously, the passive film protecting the nickel substrate, which is an ionic form of nickel, is also dissolved. Local cell action between the charged material and the nickel substrate can result in dissolution of the nickel substrate, resulting in a significant error in the determination.* As will become apparent, the error is compounded in any attempt to determine the constitutional water in the active material.

The problem of corrosion of the substrate does not occur in the analysis of the negative plate since the rest potential in both the charged and discharged state is below that at which nickel dissolution can occur.

It is worthwhile to examine the published work in this field. In most cases, the objective was a better understanding of the mechanism of the nickel electrode and of the nature of the positive active material. The analytical chemistry was for the most part only one facet of the study. In this context, the comments are quite enlightening as far as the practical problems are concerned.

Tuomi[3] in a study of the mechanism of the positive active material of pocket plate batteries made X-ray diffraction measurements paralleled by chemical analysis to determine the active oxygen content (the charged state of the positive electrode may be considered as bound active oxygen usually denoted [O]).[4] For both the X-ray measurements and the chemical analysis, it is stressed that the samples were not washed free of alkali. In the case of the X-ray measurements, the samples

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* On this same basis, oxygen which is electroreducible on a completely discharged positive plate must be rigorously excluded from the system.

were allowed to dry (with the KOH being converted to carbonate) and the nickel flake was removed magnetically. The chemical analysis for active oxygen was carried out by reaction with arsenious oxide and back titration with $KMnO_4$ without washing, and apparently, without removal of the nickel flake. As stated by Tuomi, "Samples were not washed free of electrolyte since this generally caused a slight decrease in valence state as well as decreasing the analyzed nickel content of the sample." In a further comment, when considering the more rapid rate of reaction with alcohol of an electrode directly after removal from the cell, compared to one that had been dried, Tuomi states that, "It appears certain that the valence state of 3.48 is appreciably less than is possible with the α* phase at the end of electrolysis."

Kober,[2] in his studies of positive plates by infrared spectroscopy, worked with impregnated sintered plates. Samples were prepared for spectroscopic analysis by grinding. To test whether this process altered the electrochemical activity of the sample, the powder was discharged in a pocket plate electrode and the capacity compared with a similar sintered plate. (The sintered plate was subjected to the same drying process as the powdered material.) A 25% loss in capacity was observed. Kober considered this effect to be minor from the point of view of his investigation, but it is obviously significant in any quantitative determination of the state of charge and must rule out any process that demands drying of the plate.

Aia[4] in a study of structure and stoichiometry of nickel hydroxides developed an elegant method of determining the total active material in a sintered plate using a magnetic balance. Active oxygen was determined by the iodine-thiosulphate method. According to the experimental section of the paper, the determination was carried out on dried powdered electrode material. However, for the correlation with capacity measurements, determination of active oxygen was carried out on unwashed electrodes and without the separation from metallic nickel. (Particular care is needed in carrying out the iodine-thiosulphate estimation in the presence of metallic nickel. This is discussed in the context of Harivel's work below.) Aia also noted that 80% of the active oxygen was lost in 1 hr on washing in a continuous extractor with boiling water.

Briggs and Wynne Jones,[5] and Conway and Sattar,[6] have used analytical techniques to examine thick films of nickel oxide on nickel. Conway considered

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*Tuomi uses "α phase" to designate the γ-nickel hydroxy-oxide of Glemser and Einerhand. (See the Fifth Quarterly Report for a more detailed discussion.)

that the iodometric determination used by Wynne Jones presents difficulties and notes that the metallic nickel dissolves in the acidic medium. (Bro and Cogley[7] state that the pH range must lie between 1 and 2. Above pH2, it was found that the higher nickel oxide was not completely reduced.) It is more likely, however, that dissolution of nickel is a result of interaction with the tri-iodide ion than a direct acid attack and is thus a serious source of error in the active oxygen determination. Conway's approach was to determine the extent of oxidation of an ammonical solution of hydrazine (by back titration with permanganate) by the electrode in the charged state. Careful deoxygenation was necessary to minimize the oxidation of metallic nickel. For extensive reaction times, catalytic decomposition of hydrazine to ammonia was observed. Principally for this latter reason, Conway considered the method unsuitable. The iodide method was also termed unsatisfactory. A method for determining total nickel content of the active material is, however, described by Conway in which higher valent states are reduced in hydrazine prior to dissolution in KCN to be determined spectrophotometrically.[8] Correction curves for the loss of metallic nickel as a function of immersion time in both hydrazine and the cyanide were obtained under conditions where oxygen was extremely carefully excluded from the system. (Extrapolation of these figures obtained for thin films on a wire to a sintered plaque 0.030 in. thick, 80% porous and a typical surface area of 0.12 m^2/g would result in a 2% weight loss of metallic nickel in 1 hr. For most plate extractions, it is unlikely that oxygen could be so effectively kept out of the system, so that the losses could be higher.)

Harivel [9] introduced a modification to the iodine thiosulphate approach to determine rates of self discharge of active oxides formed at different charge rates and subject to different thermal treatments. In his method, the iodine liberated by the active oxygen was titrated against thiosulphate almost immediately. The thiosulphate was added 5 ml at a time, and the time interval to the reappearance of the yellow color of the iodine noted. This technique should prevent interaction between the tri-iodide ion and the metallic nickel and eliminate the potential error in the active oxygen determination.

Kroger, [10] has recently presented methods for the determination of active oxygen and total nickel content of positive active material. The active oxygen measurement depends on reaction with a solution of ferrous ammonium sulphate. Since

this method demands washing (and in Kroger's description vacuum drying) of the electrode, it is subject to the criticism presented above that the figure obtained bears no relation to the real state of charge in the cell. The determination of total nickel was carried out by leaching with acetic acid in the presence of hydrazine sulphate.

III. ANALYTICAL METHODS

A. Introduction

Experimental studies of the composition of the active materials of the NiCd cell were started using the procedures defined by Moore[11] for the use of Muspratt solution. (The composition of this solution is typically 5 g NH_4Cl and 20 ml of concentrated NH_4OH in 70 ml water.) Analysis of negative plates proved to be straightforward. Positive plate analysis, however, showed significant corrosion of the nickel substrate.

B. Negative Plate Analysis

The discharged state of the negative plate $Cd(OH)_2$ (or CdO) may be extracted from a sintered plate using Muspratt solution. Metallic cadmium is unaffected, as is the nickel plaque at the rest potential of the cadmium electrode. The plates previously washed and dried out of contact with air and containing approximately 1 g $Cd(OH)_2$ were immersed in 200 ml of Muspratt solution at 70 to 80 °C and stirred occasionally. Additional ammonium hydroxide was added to the solution periodically to make up evaporative losses.* After 1 hr, the extraction solution was replaced, the original solution being retained in a volumetric flask. When no further weight loss was observed (as was always the case within a total of 2 hr extraction time), the plaque was removed and the extraction solutions combined. The total cadmium content of the extraction solution was then determined by titration against EDTA using Eriochrome Black T as the indicator.

The nickel plaque containing metallic cadmium was then completely dissolved in nitric acid. After the evaporation of most of acid, the residual solution was dissolved in 100 ml water and adjusted to pH 10 by the addition of NH_4OH. The total cadmium was then again determined by EDTA titration. The following procedure is necessary to determine cadmium in the presence of nickel. Both the cad-

*This is particularly important in the analysis of plates containing a nickel plated iron substrate, to prevent dissolution of the iron. In other respects, the analytical procedures described in this report are applicable equally well to plates on both nickel and iron substrates

mium and the nickel are first complexed with sodium cyanide by additing 10 ml of 10% NaCN to 10 ml of the original solution. At this time, the addition of Eriochrome Black T gives a blue color. Approximately 10 ml of formaldehyde was then added to break the cadmium cyanide complex to produce a deep red color. (Under these conditions, the nickel remains complexed.) The free cadmium was then titrated against EDTA, the end point being denoted by a purple color.

Typical analyses are listed in Table I. The first column lists the weight/unit area of the plate after impregnation. Separate determination of $Cd(OH)_2$ and Cd by the technique described above gives the figures listed in columns 2 and 3. Combining these two figures gives the total weight of active material which we may subtract from column 1 to provide the weight/unit area of the plaque (column 5). This can be compared with the weight/unit area of the plaque prior to impregnation (column 6). Good agreement is obtained even though six separate physical measurements are involved. There is an indication of a small systematic error in that values (with one exception) recorded in column 5 are higher than in column 6. It is worth noting the importance of chemical analysis in assessing plate uniformity. For the first two samples, there is a 4% difference in the total weight of active material as cadmium and cadmium hydroxide, but the agreement is better than 1% when measured as total Cd content. The figures also indicate that there is little corrosion of the nickel plaque in the impregnation of negative plates by the Fleischer method.* Since no extensive efforts were required to develop the techniques to a satisfactory level of accuracy, not further results will be catalogued here. The analyses carried out routinely to determine utilization as a function of the method of impregnation will be presented later.

C. Positive Plate Analysis

The principal problem in positive plate analysis, as discussed in the introduction, is to ensure complete extraction (separation) of the active material from the nickel plaque without simultaneously dissolving the plaque. In the presence of air or any active material in the charged state the rest potential of the plate is such that the dissolution of metallic nickel is prevented only by the presence of a passive film of nickel oxide. Since the common methods of extraction of the active material, using complexing reagents, also result in dissolution of the passive film, corrosion of the nickel substrate is a very real potential error in the determination.

To assess the practical significance of the problem, we examined the straightforward application of the Muspratt extraction technique, as described by

*See Ref. 1 for discussion of impregnation methods.

Table I Check on Analytical Methods for Negative Plates

(1)	(2)	(3)	(4)	(5)	(6)	(7)
			Total Weight of Active Material, g/cm^2			
Plate Weight, g/cm^2	$Cd(OH)_2$, g/cm^2	Cd Content, g/cm^2	(2 + 3) As Cd + $Cd(OH)_2$	As Cd	Plaque Weight, g/cm^2 (1 − 4)	Plaque Weight Prior to Impregnation, g/cm^2
0.2332	0.0384	0.0171	0.0555	0.0466	0.177	0.170
0.2262	0.0264	0.0269	0.0533	0.0472	0.163	0.165
0.2978	0.0786	0.0483	0.1269	0.1188	0.171	0.167
0.2985	0.0579	0.0697	0.1276	0.1142	0.171	0.167
0.3429	0.1221	0.0447	0.1668	0.1383	0.176	0.166
0.3325	0.1379	0.0259	0.1638	0.1319	0.169	0.165
0.3575	0.1080	0.0811	0.1891	0.1642	0.168	0.165
0.3604	0.1142	0.0772	0.1914	0.1648	0.169	0.165
				Mean values:	0.170	0.166

Moore,[11] to physical mixtures of $Ni(OH)_2$ and carbonyl nickel powder of well defined composition. The $Ni(OH)_2$ was carefully dried. X-ray determinations indicated that it contained no water.

The analysis was carried out as follows. The extraction solution was prepared by dissolving 10 g ammonium chloride in 250 ml of distilled water and the solution warmed to 80 °C. Seventy-five ml of 28% ammonium hydroxide was then added. The sample was immersed in the extraction solution and the temperature maintained at 80 °C. The extraction of active material was allowed to proceed for 3 hr. Approximately 25 ml of 28% ammonium hydroxide was added for each hour of the extraction. The whole process was then repeated several times with fresh extraction solution until no further coloration was observed. Finally the sample was washed, dried, and weighed. The amount of active material was determined from the net weight loss. The results obtained for mixtures containing 40 and 50% nickel hydroxide and for 100% nickel powder are given in Table II. (The 40 and 50% mixtures are close to the ratio of active material to nickel plaque in a typical positive electrode.) The observed weight loss for both the 50% mixtures examined gave an apparent active material content of 60.1%. For the mixture containing 40% active material, the apparent content was 50.0%. In both cases, there is a positive error of approximately 10% which must be attributed to corrosion of the nickel. The weight losses for the two samples of pure nickel powder exposed to the extraction solution for the same period of time resulted in substantial weight losses, 14% for the Type 287 powder and 18.4% for the higher surface area Type 255 powder. Reduction of the surface oxide in H_2 at 600 °C showed only a 1.3% loss in weight. The lower percentage weight losses observed for the physical mixtures, as opposed to the pure nickel powders, is probably a result of masking of the nickel surface by the finely divided $Ni(OH)_2$. This effect would result in some protection of the nickel substrate in a positive plate, but it is still considered that the corrosion would be significant.

A further criticism of the method is that, since the stoichiometry of the active material is ill-defined (particularly after it has been cycled), the determination of the weight loss cannot give an atom % Ni figure for the active material. This number is essential to a calculation of charge efficiency or utilization.

Also in these preliminary studies, measurements were carried out on positive plates (in the discharged state) removed from an aerospace cell, but in this case the extraction solution was 0.5% KCN out of contact with air. This extraction process is based on a method due to Brummet and Hollweg[8] for the determination of oxide films on nickel. It has the advantage that the quantity of nickel in solution is very conveniently determined spectrophotometrically, as the cyanide. The ultra-

Table II. Analysis of Physical Mixtures of $Ni(OH)_2$ and Carbonyl Nickel Powders

Sample	Method	Apparent Wt % Ni(OH)
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
40% $Ni(OH)_2$, 60% Ni (287)	Muspratt	50.0
		Weight Loss
100% Ni (287)	Muspratt	14.0
100% Ni (255)	Muspratt	18.4
100% Ni (255)	Reduction in H_2 at 600 °C	1.3

violet absorption at 286 mμ obeys Beer's law over a wide range of concentrations. However, the weight losses observed in the extraction process never reached a plateau value, i.e., continuous corrosion of the nickel substrate occurred resulting in values as high as 63.4% (see Table III) for the active material. (Subsequent analysis of similar plates under conditions where nickel dissolution could not take place showed an active material content between 35 and 45%.) Two extractions carried out with Muspratt solution also showed high values for the weight loss.

Table III. Analysis of Positive Plates from Aerospace Cell

Sample No.	Extraction Method	Extraction Time, Hr	Weight Loss, %
1a	KCN	4	49.0
1b	KCN	30	63.4
2a	KCN	4	48.9
2b	KCN	25	54.2
3	Muspratt	4	55.4
4	Muspratt	4	54.5

Exclusion of air from the solution during the extraction of these positive plates did not produce a significant difference in the weight percent loss. This was attributed in part to the presence of adsorbed oxygen on the high surface area active material and to the fact that the positive active material can never be discharged completely to the divalent form. (The undischarged material becomes activated as the protective film of $Ni(OH)_2$ is dissolved during extraction.) The straightforward Muspratt extraction or extraction with KCN are therefore considered unsuitable methods of determination of the active material in the positive plate.

Two modifications to the method were considered. The first of these was to carry out the extraction in the presence of a reducing agent that would, in theory, remove the electroreducible species which are a necessary adjunct to the nickel corrosion process.

The materials examined were hydrazine and sodium borohydride. In the first case, the hydrazine was found to be ineffective possibly because of the high pH of the Muspratt solution. A separate pretreatment with hydrazine at lower pH followed by extraction in Muspratt solution resulted in significant losses of active material by complexation with hydrazine.

This need not have been an obstacle to the development of an acceptable method but the procedure defined below is considered to be more effective and straightforward. Since this work was carried out, a method of positive plate analysis using acetic acid in the presence of hydrazine has been published,[10] but it does require that the electrode be crushed and the metallic nickel be removed magnetically prior to dissolution.

In the case of sodium borohydride, it was found that spontaneous decomposition occurred and that the extraction process was complicated by side reactions with the decomposition products.

The second modification of the basic method to counteract the effect of the presence of electroreducible species involved potentiostatting the positive plate at a low positive potential during the extraction process. The first step in defining this technique was to establish the potential range in which no nickel dissolution could occur. A current potential scan was carried out on a pure nickel plaque in Muspratt solution containing divalent nickel.

The 5 cm^2 plaque was first held at 0.0 V versus RHE while N_2 was bubbled through the solution. The initial cathodic current corresponding to reduction of dissolved O_2 decayed to less than 0.1 mA/cm^2 in a matter of minutes. This small cathodic current was maintained up to a potential of ~+100 mV versus RHE when the current became anodic. The anodic current then increased until, at +300 mV versus RHE, it reached a value of 5 mA/cm^2. This value subsequently decreased for further increase in potential but remained significant at ~1 mA/cm^2 (see Fig. 1). From this behavior, we may deduce that the passive film normally formed on nickel at potential between 200 and 300 mV versus RHE is not stable in Muspratt solution. However, below +100 mV versus RHE, no dissolution of nickel takes place. We considered the possibilities that: (1) as the concentration of nickel increased during the extration process, nickel might be electrodeposited from solution, and (2) further reduction of the discharged active material to metallic nickel could also occur. With regard to the latter point, Kronenberg[12] has reported that reduction of $Ni(OH)_2$ does not take place until the H_2 evolution potential is reached. In practice, we have found that, at +25 mV versus RHE, we observed a cathodic current of between 2 and 4 mA for a 5 cm^2 plate. This current was most probably due to oxygen reduction, but even if it corresponded to nickel deposition (from either process listed above) it would result in only 10 mg weight increase in the normal extraction time of 5 hr, i.e., less than a 1% error in the extraction of a 5 cm^2 plaque that weighed approximately 1 g.

With the opportunity to ensure complete extraction of active material without the risk of corrosion of the substrate, it is possible to determine with a reasonable

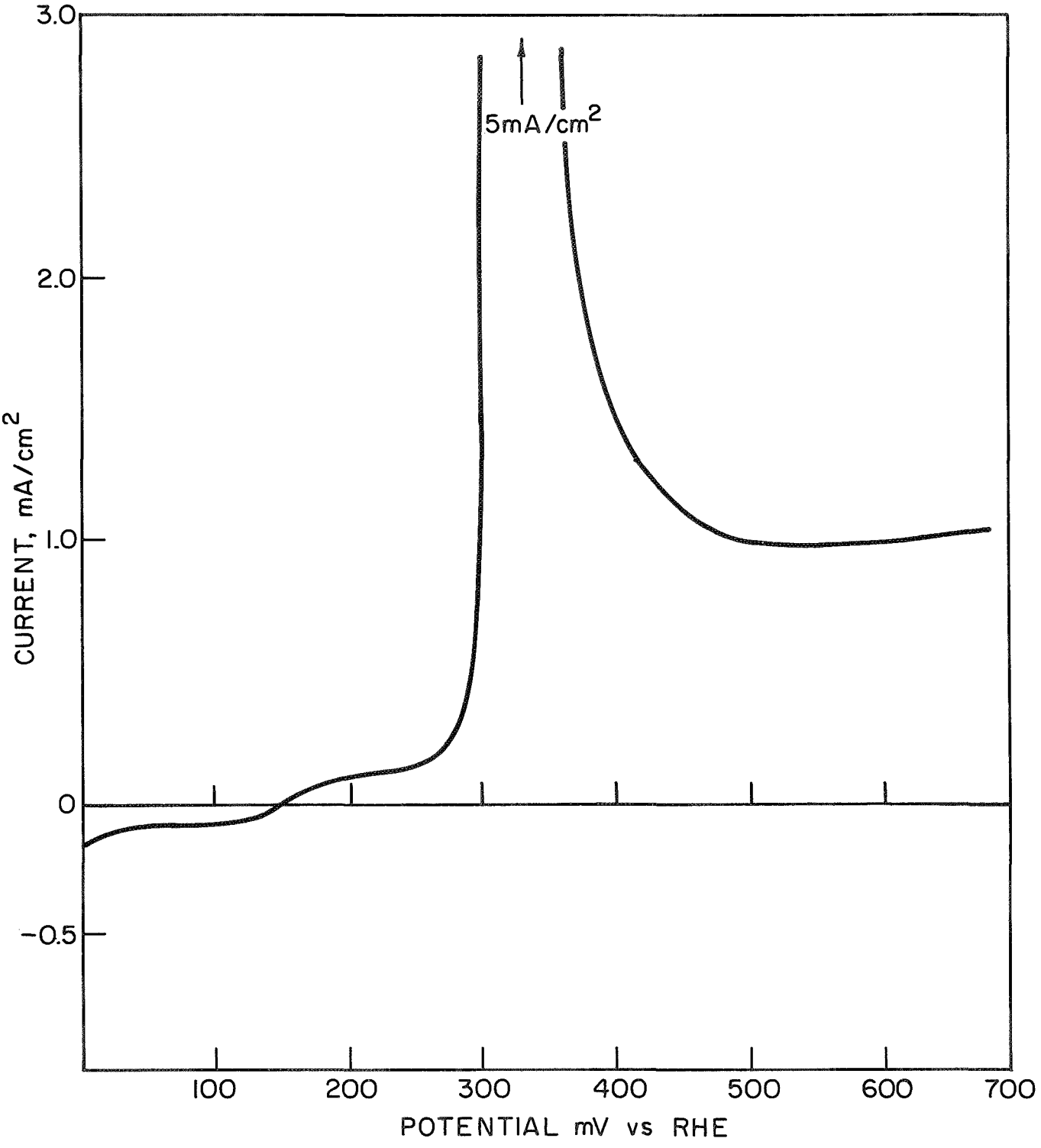

Fig. 1. Current-voltage curve for nickel plaque in Munspratt solution

degree of accuracy the crystalline water content of the active material. The significance of the water content in terms of utilization and charge acceptance will be discussed in detail in the future. At this time, it is sufficient to note that this is an important aspect of positive plate analysis. Water content is determined by comparing the weight loss on extraction with the total nickel content of the extraction solution determined by dimethyl glyoxime. The procedure, for a plate of known weight and approximately 5 cm^2 in area, is to immerse in 175 ml of Muspratt solution at 70 °C in a four-necked flask under potential control (Fig. 2). A dynamic hydrogen reference electrode,[13] set up behind a glass frit, was used to establish the positive plate at a potential of 25 mV versus RHE. The counterelectrode of Pt, also behind a frit, was inserted in the third neck of the flask. Nitrogen was bubbled through the solution to minimize the effect of the oxygen evolved at the counterelectrode on the extraction process. The extraction solution took on a distinct blue color within 20 to 30 min and was routinely replaced with fresh solution after 1 hr. The extraction process was continued for 4 hr or longer if the blue coloration persisted. The nickel content of the combined extraction solutions was determined by precipitation with dimethyl glyoxime. The plaque after extraction was carefully washed, dried, and weighed to determine the total weight loss. Comparison of the weight/unit area after extraction with the weight/unit area of the plaque prior to impregnation gives a measure of the extent of plaque corrosion that took place during impregnation or cycling. As defined above, the water content of the active material is calculated from the weight of active material extracted and the nickel content as determined by dimethyl glyoxime. For $Ni(OH)_2 \cdot 1.5\ H_2O$ stoichiometry [α $Ni(OH)_2$] the water content would be 22.6% for $Ni(OH)_2 \cdot H_2O$ 16.8% and for $Ni(OH)_2 \cdot 0.5\ H_2O$ approximately 9%.

In Table IV, some of the more interesting results are set out. Samples 1a and 1b were adjacent pieces cut from the same plate; sample 1a was examined without control, for 1b the potential was maintained at 25 mV versus RHE. The results indicate that in the case of the green plate (i.e., prior to formation and cycling) there is not too great a problem in analyzing for active material content and that potential control is not essential (as long as air is carefully excluded). Very good agreement was obtained for the two determinations; it is interesting to note that the plaque weight after extraction is some 5% lower than the plaque weight prior to impregnation. Since these plates were not cycled, this weight loss must represent the extent of corrosion of the plaque during the impregnation process.

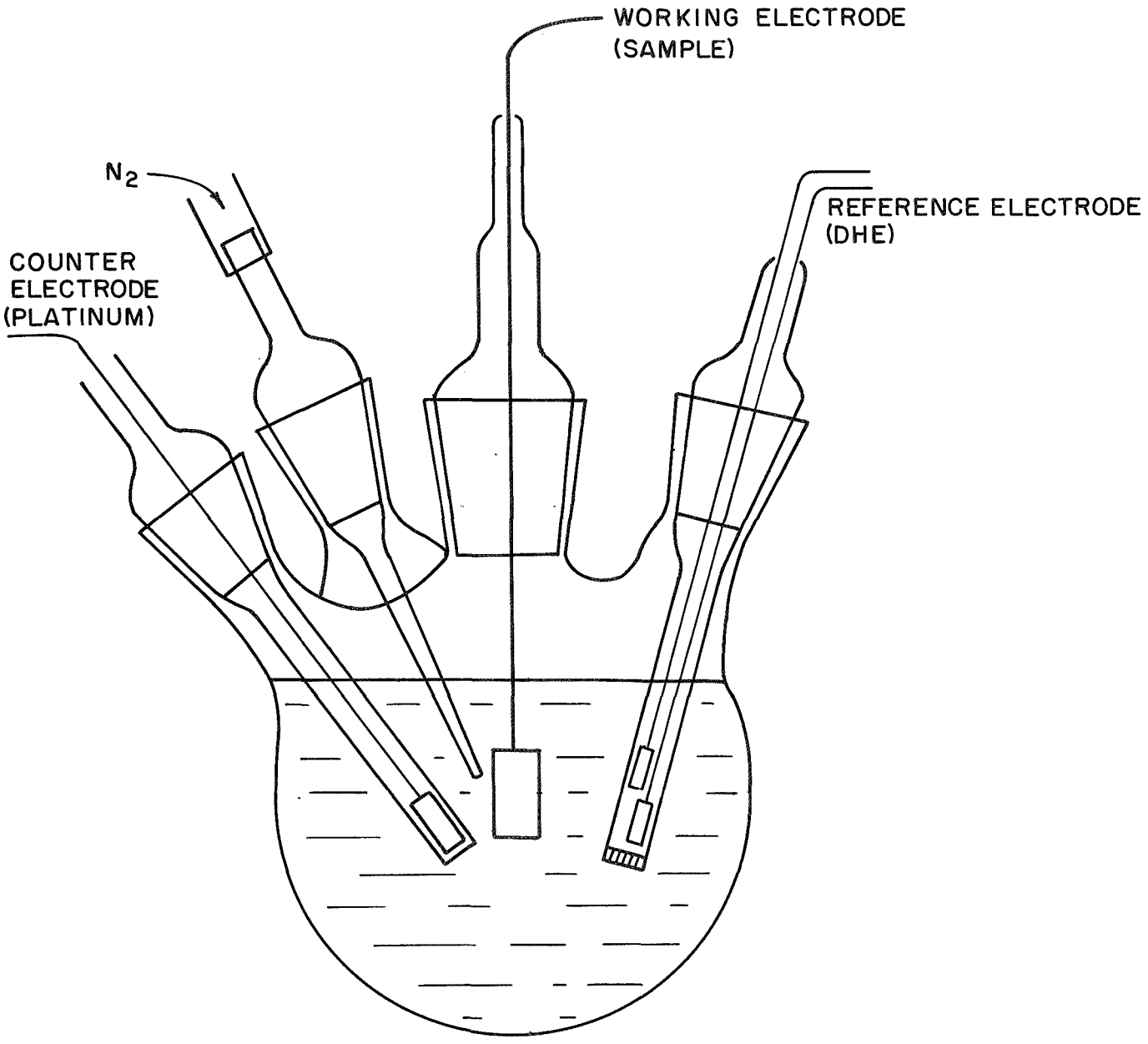

Fig. 2. Extraction of active material from possitive plate under potential control

Table IV. Analysis of Positive Plates

Sample	Comments	Potential Control During Extraction*	Plate Wt Before Extraction, g/cm^2	Plaque Wt, g/cm^2 After Extraction	Plaque Wt, g/cm^2 Before Impregnation	% Wt Loss on Extraction	% $Ni(OH)_2$ by Analysis	% H_2O in Active Material
1a	Green plate	No	0.2309	0.1931	0.2036	16.4	15.0	9
1b	Green plate	Yes	0.2300	0.1907	0.2036	17.0	15.0	13
2a	Cycled plate in discharged state†	No	0.2067	0.1670	0.1750	19.2	19.2	—
2b	Green plate†	Yes	0.2133	0.1769	0.1750	16.8	17.2	—
3a	Green plate†	Yes	0.2530	0.2046	0.2036	19.1	19.3	—
3b	Cycled plate in discharged state†	Yes	0.2503	0.2004	0.2036	19.9	19.3	(3)
4	Green plate	Yes	0.2448	0.1922	0.2027	21.7	21.6	—
5	Cycled plate in discharged state	Yes	0.2464	0.1915	0.2027	22.3	18.7	15

* Extraction in Muspratt solution at 70 °C, potential control at 25 mV versus RHE.

† Plates impregnated by Fleischer method without nitric acid in impregnation solution.

In contrast, samples 2a and 2b demonstrate the requirement for potential control once the plate has been formed or cycled. The percentage weight loss of sample 2a is some 2.5% greater than 2b. This can only be attributed to plaque corrosion since these are adjacent samples from a plate of uniform weight distribution. The extent of corrosion is also reflected in an apparent increase in the percentage $Ni(OH)_2$ in the plate as calculated from the Ni^{2+} content of the extraction solution. For sample 2b extracted under potential control, the plaque weight after extraction was almost identical to that of the plaque prior to impregnation. Note that both the plates used for samples 2 and 3 were prepared by an impregnation method that did not use nitric acid in the impregnation solution, so that little corrosion of the plaque would be expected. Samples 3a and 3b demonstrate the degree of improvement in the analysis of a discharged plate when the active material is extracted under potential control. In this case, there is excellent agreement in the determination of Ni content in the active material. The slightly greater weight loss observed for 3b can probably be attributed to an increased water content in the active material that was cycled. Samples 1 through 3 were listed to make the specific points above. Samples 4 and 5 are typical examples of results obtained routinely. Note that despite good agreement for the weight per unit area of these plates and the uniform weight loss, the actual Ni^{2+} content of the active material is significantly different. Some corrosion of these plaques is evident during impregnation.

It is apparent from the data presented in Table IV that the determination of the water content from the difference between weight loss and direct determination of Ni^{2+} cannot have a high degree of accuracy. However, the figures presented are not considered typical since no special precautions were taken to ensure reproducible drying conditions from sample to sample. Furthermore, for cycled plates, it is necessary to define the K^+ content of the active material since this will also contribute to the weight loss and would be a source of error in the determination of water content. In principle, therefore, it is possible to determine the water content, of the positive active material though no concrete examples of the technique are presented here.

In more general terms, the conclusions we may draw are that this technique of extraction of positive active material under potential control provides a quantitative method for the determination of:

1. The amount of active material in a positive plate
2. The atom % Ni^{2+} in the active material
3. The extent of plaque corrosion, both in impregnation and on cycling.

The one limitation is that analysis under potential control can only be carried out with plate in its lowest possible state of charge.

D. Determination of State of Charge of the Positive Plate

A capability to determine the quantity of active material in a positive plate as described above is useful in assessing the uniformity of an impregnation process. It does not, however, provide enough information to calculate the utilization of the active material since the stoichiometry of the charged state is nonintegral (as is the discharged state after cycling). Since both the stoichiometry and the distribution of the active material could be functions of the impregnation process and conditions, it is desirable to be able to define which impregnation process and which conditions give rise to the most uniform and predictable behavior, i.e., a method of determining the state of charge is required. For reasons that will become apparent, rigorous definition of the state of charge is probably not attainable; the problem again is one of an error caused by corrosion of the substrate. However, this error can be minimized if certain experimental precautions are taken. Then, if it is assumed that this systematic error is a relatively consistent one, a useful analytical method is available for comparative purposes.

The state of charge is commonly defined in terms of its active oxygen [O] equivalent. The standard method of determining active oxygen is to liberate iodine from a slightly acid solution of potassium iodide, then to titrate the free iodine (present as I_3^-) against a standard solution of sodium thiosulphate.

In the following we will present the problems that occur in practice when this method is attempted and also discuss the precautions that can be taken to alleviate them. In the initial experiments, the procedure started with washing and drying the plate, followed by immersion in 25 ml of a sodium acetate buffer at pH 4.5 (20 g sodium acetate and 15 ml of glacial acetic acid made up to 200 ml) containing 5 ml of 25 wt % Kl solution. The flask was then sealed and left overnight. The free iodine was titrated against 0.05N sodium thiosulphate using starch as an indicator at the end point. Typical results are listed in Table V. Note that separate determination of the $Ni(OH)_2$ content of the plate by the method described above is necessary. The procedure adopted was to use a 10 cm^2 sample of plate and use approximately half the sample for the $Ni(OH)_2$ determination and half active for [O] measurement (uniform distribution is assumed for this size of sample). The apparent nickel valence was calculated from the mole ratio of [O] to $Ni(OH)_2$ assuming an equivalent weight of 8 for [O].

Table V. Preliminary Determinations of State of Charge

Sample	Wt/unit Area, g/cm^2	Wt % $Ni(OH)_2$	Wt %[O] in Active Material	Apparent Ni Valence*
Green plate	0.2113	17.2	0.39	2.04
Charged state	0.2067	19.2	3.38	2.39
Charged state	0.2055	14.0	3.56	2.42

* Calculated from nickel valence = $2 + \frac{2 \text{ mole [O]}}{\text{mole } Ni(OH)_2}$.

It is immediately obvious that the apparent nickel valence in the charged state determined by the method detailed above is too low. Capacity measurements assuming 1F/mole $Ni(OH)_2$ and 100% utilization indicated that the valence should be in excess of 3. (It should also be noted that the three samples listed in Table V were not in any way related and were not intended to be a test of reproducibility.)

Several effects were examined at this time to try to explain the low values, these included:

1. The extent of overcharge
2. KOH concentration
3. The number of cycles
4. Time of reaction between charged plate and KI.

These results will not be included since the values obtained showed little improvement. However, the trends observed did help to define improved analytical procedures. The active oxygen content in contrast to the results reported by Aia[4] did not show an increase with the extent of overcharge. Plates charged to 100%, 200%, and 300% exhibited random behavior giving rise to apparent Ni valencies of between 2.4 and 2.5. Increasing the concentration of KOH during the charging process from 25 to 30% showed an increase in active oxygen content of approximately 20%.

These two factors pointed to the serious source of error associated with self discharge in the washing and drying process, particularly during the washing. There was also an apparent increase in active oxygen content on cycling even though the measured discharge capacities were approximately constant. It is now con-

sidered that this is an artifact of the analytical procedure, possibly related to self-discharge rates, which could vary significantly in the first few cycles.

Interesting information was also obtained in the examination of the effect of contact time between the charged positive plate and the acidified KI. The pattern of the results is shown in Fig. 3. The apparent active oxygen content increases with time up to 6 hr. It then decreases at a somewhat slower rate in an approximately linear fashion. Note that there is a significant decrease in [O] between the maximum figure at 6 hr and the 16 hr (overnight) routinely used in the procedure discussed above. (The values are still low in comparison to the discharge data, because these plates were washed and dried before analysis.) The lower value obtained for the active oxygen content after long reaction times is considered to be due to the reduction of I_3^- by metallic nickel. The charged plate is at a potential where the metallic nickel substrate would normally be protected by a passive layer of nickel oxide. However, in the presence of acetate ions which can complex Ni^{2+} or even possibly potassium iodide, this passive film is attacked and nickel dissolution can occur. The accompanying cathodic process could be either discharge of active material or reduction of I_3^-. From the experimental behavior depicted in Fig. 1, the latter reaction must occur; it is also possible that the former reaction also occurs. The extent to which the active material is discharged is the systematic error referred to in the preliminary discussion beginning this section. It will be considered in more detail below.

As a result of the evidence presented above, two modifications were introduced in the analytical procedure. The first was the elimination of the washing and drying step. Plates were transferred immediately on completion of the charge or overcharge process into the iodide solution, i.e., self discharge on dilution and spontaneous self discharge on open circuit in KOH were kept to a minimum. In contrast to the washing process in which bubbles of oxygen are formed quite rapidly, immersion in the iodide solution did not result in gassing.

The second improvement in the basic technique follows a recommendation of Harivel.[9] Accumulation of I_3^- in solution during the reaction with the positive plate is prevented by regular addition of sodium thiosulphate. As soon as the pale straw color associated with free iodine is apparent, a known small volume of thiosulphate is added. This procedure is followed until the reaction is complete. For a 1 g sample, the total reaction time is 6 to 7 hr. The end point for the thiosulphate titration was determined in the presence of starch. Note that in the latter part of the reaction it is important not to add too much thiosulphate.

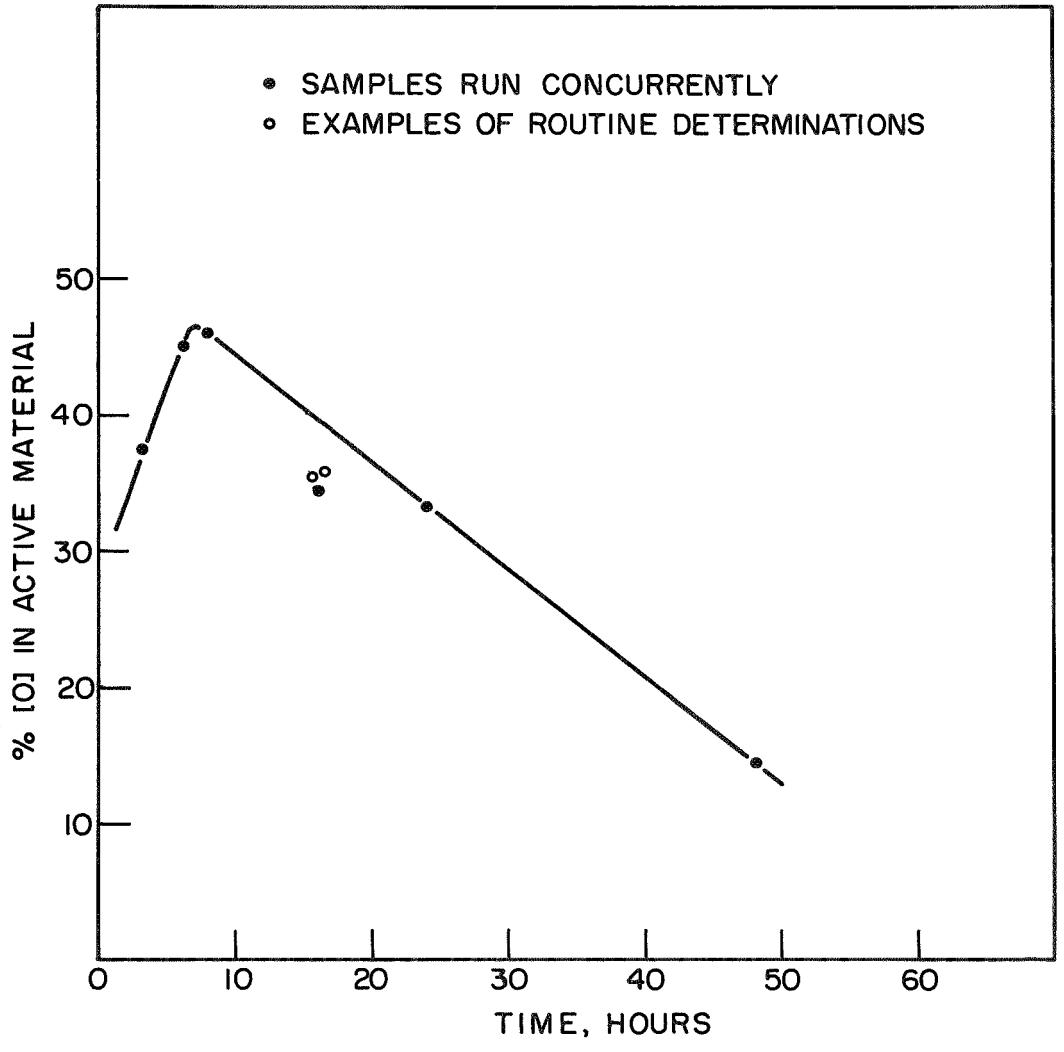

Fig. 3. Variation of apparent active oxygen content as a function of contact time with acidified KI

In practice the first improvement in the elimination of washing and drying was put into effect before the latter. The results shown in Table VI show the marked effect of this change. The values for the active oxygen content are, however, still considered to be too low because of the very long contact times with the iodide.

Table VI. Effect of Washing and Drying of Sample on Active [O] Determination

Sample	Weight per unit Area, g/cm^2	Wt % $Ni(OH)_2$	Wt % [O] in Active Material* Washed and Dried	Direct Transfer
1	0.2503	19.1	4.35 (2.50)	6.97 (2.80)
2	0.2008	13.1	4.36 (2.50)	8.27 (2.95)

* Figures in parenthesis are corresponding apparent nickel valencies.

When the second improvement was put into effect, the measured values for the active oxygen content showed a further increase to nearly 10% by weight of the active material. The revised procedure was then to transfer the plate, on termination of the charge or overcharge process, directly into the iodide solution and to add 5 ml of 0.025N sodium thiosulphate each time the color of free iodine was apparent in the solution. Initially, these additions were made at approximately 15-min intervals, but lengthened considerably as the reaction proceeded. Some typical results obtained by this method are presented in Table VII.

The first point to establish from the results is that reasonable reproducibility is achieved with this technique. See for example samples 5, 6, and 7. However, in comparison with measured capacities, the values obtained for the apparent nickel valence are too low. Consider for example sample 5. This sample contained 0.134 g of active material, determined as $Ni(OH)_2$ on an adjacent piece of the plate in the discharged condition. We may then calculate a theoretical capacity based on the apparent nickel valence of 3.0 in the charged state and 2.2 in the discharged state (from the figures of Table VII). This value is 0.031 Ahr. Since the measured capacity to a 1.0 V cutoff was 0.0385 Ahr, the analytical determination of the valence of the charged state must still be too low.

Table VII. Apparent Ni Valence as Function of Charge, Overcharge, and Overdischarge

Charged State

Sample	% Charge at C/2 Rate	Wt % [O] in Active Material	Apparent Ni Valence
1	50	6.0	2.69
2	100	7.5	2.87
3	150	7.5	2.87
4	200*	8.25	2.96
5	200	8.95	3.04
6	200	9.25	3.07
7	200	9.35	3.08
8	1000	9.75	3.13

Discharged State

Sample	Time of Over-discharge, Min	Wt % [O] in Active Material	Apparent Ni Valence
9	0	3.2	2.37
10	5	2.7	2.31
11	15	1.8	2.21

*20 min stand at open circuit prior to analysis.

The results otherwise show a high degree of internal consistency. The apparent valence increases with the extent of overcharge. The charging process up to 50%* is demonstrated to be much more efficient than the latter stages. The same apparent nickel valence is observed for the 100% charge and 150% charge. This probably reflects a greater attack on the nickel substrate for the more highly charged plate. The small loss in capacity generally observed on open circuit stand is confirmed by a smaller active oxygen content for sample 4, compared to samples 5, 6, and 7.

The somewhat high values of the valence in the discharged state can probably be attributed to hysteresis at the relatively rapid C/2 discharge rates used in these experiments. Overdischarge for 15 min results in a more acceptable value.

In view of the fact that the active oxygen determination in the charged state is still low, it is difficult to define active material utilization precisely. The active oxygen content of the discharged state gives some measure of material not cycling, but there are no means to determine whether any divalent nickel is present in a fully charged plate.

As a footnote, it might be added that attempts were made to follow weight changes in the positive plate during charge and discharge cycles, the objective of determining the extent of hydration of the charged active material. (A separate determination of the K^+ content was envisaged.) The results obtained using a Cahn electrobalance showed considerable hysteresis, and very complex oscillatory phenomena, in relatively small changes in weight. Time did not permit rigorous pursuit of this behavior.

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*Based on discharge capacity observed in previous cycle after 100% overcharge.

IV. STUDY OF IMPREGNATION PROCESSES

Work was commenced on the following program to study specific variables in three different impregnation methods (the basic principles of the methods were discussed in the previous report).

A. Chemical Conversion

Positives

saturated $Ni(NO_3)_2$ + nitric acid, 25% KOH at 80 °C

— 2, 5, 8, and 12 impregnation cycles

50% saturated $Ni(NO_3)_2$ + nitric acid, 10% KOH at 80 °C

— 2, 5, 8, and 12 impregnation cycles

Negatives

saturated $Cd(NO_3)_2$ + nitric acid, 25% KOH at 80 °C

— 2, 5, 8, and 12 impregnation cycles

50% saturated $Cd(NO_3)_2$ + nitric acid, 10% KOH at 80 °C

— 2, 5, 8, and 12 impregnation cycles

B. Fleischer Method[14]

Positives

saturated $Ni(NO_3)_2$ + nitric acid, 25% KOH at 80 °C

— 2, 5, 8, and 12 impregnation cycles, cathodized at 150 mA/cm^2

— 2, 5, 8, and 12 impregnation cycles, cathodized at 300 mA/cm^2

Negatives

saturated $Cd(NO_3)_2$ + nitric acid, 25% KOH at 80 °C

— 2, 5, 8, and 12 impregnation cycles, cathodized at 150 mA/cm^2

— 2, 5, 8, and 12 impregnation cycles, cathodized at 300 mA/cm^2

C. Electrochemical Conversion

Positives
- saturated $Ni(NO_3)_2$, 25 °C
- cathodized at 0.17 A/cm^2, 0.34 A/cm^2, and 0.68 A/cm^2 for 5, 10, and 20 min, respectively

Negatives
- saturated $Cd(NO_3)_2$, 25 °C
- cathodized at 0.17 A/cm^2, 0.34 A/cm^2, and 0.68 A/cm^2 for 5, 10, and 20 min, respectively

Each plate preparation will be carried out in duplicate to check the reproducibility of the method and the uniformity of weight gain and capacity. The effect of loading and the extent of corrosion of the substrate on uniformity and efficiency will be examined in detail. The information gathered in this program will be presented and analyzed in the next quarterly report.

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